The Nitro Group as Substituent

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1 Introduction

If a structural unit is denoted as a 'substituent', this usually has one of the two following meanings:

(1) The substituent is a smaller part of a molecule which can be introduced by a simple chemical operation, particularly when it can directly replace a hydrogen atom.

(2) The substituent is a smaller and less important part of a molecule which influences the properties of the molecule in a quantitative sense but does not alter its general chemical character: the latter is controlled by another group present: the functional group[1] (or the reaction site).

The nitro group is a substituent *par excellence*, both typical and important, according to either definition. For instance, 4-nitrophenol will be viewed in most circumstances as a substituted phenol, much less often as a substituted nitrobenzene. It can be prepared easily from phenol, but not simply from nitrobenzene. Its chemical and physicochemical properties are more closely related to those of phenol than to those of nitrobenzene. This view, however, may change if an appropriate physicochemical property is studied. For instance in electroreduction the nitro group will act as the functional group.

On the other hand, the nitro group is a 'strong' substituent since the differences in acidity, reaction rates and spectral shifts between nitrophenol and phenol are large compared to the effects of other substituents.

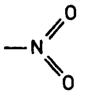
In this review the term nitro group is used in a narrow sense as NO_2 bonded to a carbon atom. We shall deal only with the second aspect of substitution, and particularly with the quantitative measures of the substituent strength estimated by substituent constants σ[1–3] as well as by other parameters; the electronic and geometric structure of the nitro group must be also mentioned. We give much attention to nitrobenzene since it has been more extensively investigated than any other nitro compound.

Otto Exner, born in Praha, formerly Czechoslovak Republic, received a PhD degree from the Institute of Chemical Technology in 1951 and a DSc degree from the Czechoslovak Academy of Sciences in 1961. He has worked in several Institutes of this Academy, and has been forced several times to change his employment on political grounds, and partly also because his interests lay between organic and physical chemistry. He has lectured at several Universities in Czechoslovakia, since 1969 as Professor of Organic Chemistry, and has had appointments as visiting Professor in Italy, Sweden and France. His main scientific interest is in correlation analysis, particularly the Hammett equation, isokinetic relationships, and reactivity–selectivity principles: secondary interests are dipole moments, conformations and hydroxylamine derivatives.

2 Properties and Electronic Structure of the Nitro Group

The nitro group may be derived formally from N_2O_4 which is a strong oxidizing agent. If the nitro group is attached to a hydrocarbon of any kind, it changes the electron affinity of the molecule significantly. Alkanes and benzene are not reduced electrochemically, whereas their nitro derivatives are, with rather low values of formal potentials of reduction.

The earlier formulated structure **1** of the nitro group has been replaced by the resonance of two degenerate forms **2** ↔ **3** which describe in a somewhat cumbersome way the simple fact that the two oxygen atoms are equivalent. In particular also the canonical structure **4** comes into consideration; its significance is that the second positive charge is delocalized over the moiety to which the nitro group is attached. The formally positive charge on the nitrogen atom explains the strong electron-attracting power of the whole substituent. This is manifested by the high value of the group electronegativity and of the dipole moments (see later sections). Recently also a contribution from the biradical form **5** was considered[4] and estimated in the case of *p*-nitro derivatives of aniline and phenol to be significant.[5] Even the old structure **1** could again be taken into account since in fact the NO bond lengths are required for a double bond.[4] For chemical consequences the form **4** is particularly important and instructive; it is postulated in textbooks, but its weight in *p*-nitrophenol and *p*-nitroaniline was found recently[5] to be only about 1%. This is in line with many other theoretical and experimental studies of nitrobenzene and its derivatives,[6–9] which all have shown a limited importance of the form **4**.



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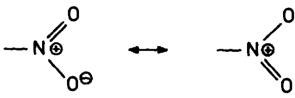

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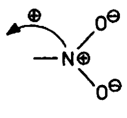

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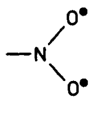

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Tadeusz Marek Krygowski was born in Poznań, Poland and received his PhD degree in 1969 and a DSc degree in 1973, both from the Department of Chemistry of Warsaw University. Since 1964 he has been working at this University, from 1983 as a Professor of Chemistry. He has lectured at many universities in many countries, serving as an invited Professor in Canada and France. Elected as president of the Polish Chemical Society in 1994, his main interests are: ion-pairing in organic electrochemistry, solvent and substituent effects, structural organic chemistry, and studies on aromaticity.

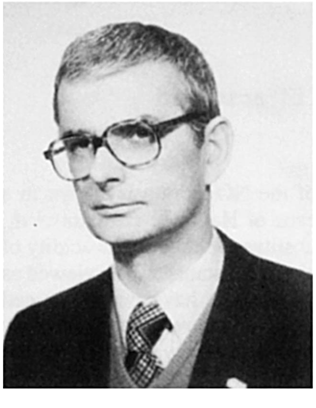


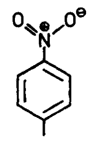
Table 1 Geometry of the nitro group attached to various moieties

Molecule	Bond length (d/Å)			Bond angle (°)
	CN	NO	NO	ONO
Nitrobenzene,[10] ED[a]	1.486(2)	1.2234(4)		125.32(8)
Nitrobenzene,[11] XD (low temp.)	1.467(1)	1.227(1)		123.2(1)
Corrected for liberation	1.477	1.229	1.233	
p-Nitroaniline,[12] XD	1.434(2)	1.227(2)		121.6(2)
N,*N*-Diethyl-*p*-nitroaniline,[13] XD[b]	1.437(5)	1.234	1.223	121.9(3)
	1.429(5)	1.221	1.232	121.7(4)
Corrected for liberation	1.441	1.243	1.232	
	1.434	1.229	1.241	
p-Nitrophenolate anion[9] XD	1.418(5)	1.241(2)	1.247(2)	
Nitromethane,[14] MW	1.489	1.224		125.3

[a] XD: X-ray diffraction; ED: electron diffraction; MW: microwave measurements.
[b] Two independent molecules in the asymmetric unit.

3 Geometry of the Nitro Group

The geometry of the nitro group does not depend significantly on the nature of the moiety to which it is attached. Data collected in Table 1 present this clearly. The most sensitive parameter is the length of the C−N bond, which may serve as an approximate measure of the resonance effect of the nitro group, interacting *via* this bond with the moiety to which it is attached. Thus if a partial CN double bond is induced, it means that the canonical structure **4** contributes significantly to the description of the molecule. The C−N length in nitrobenzene is almost the same as in nitromethane, in spite of the sp^3 character of the C atom in the methyl group. In electron diffraction[10] or low-temperature X-ray diffraction measurements[11] on nitrobenzene on the one hand, and microwave determination of the geometry of nitromethane[14] on the other, the difference is statistically insignificant. It might be concluded that the resonance effect of the nitro group in nitrobenzene is very low or even practically zero. In other words, the structure is described sufficiently by the canonical structures **6** and **7** while structures **8**—**10** have low weights. As mentioned this need not apply when the nitro group is attached to strongly electron-donating moieties; then structure **11** may be of importance.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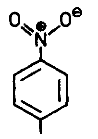
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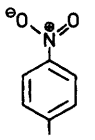
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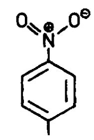
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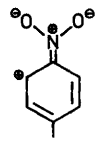
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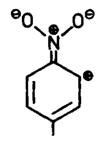
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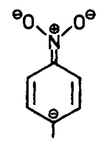
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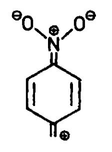
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4 Electronic Substituent Effects and Substituent Constants

4.1 Hammett Constants

The electron-attracting character of the NO$_2$ group is shown in a simple and convenient way by means of Hammett constants,[3] σ_m and σ_p. Defined originally as the substituent effect on the acidity of substituted benzoic acids in water, these constants can be viewed as experimental quantities. Subsequently, they have been obtained also from other reactions or as statistical mean values from many reactions.[1] Table 2 gives some examples and the values agree quite well. The electronic effect of NO$_2$ is thus regular and well predictable. In addition it is strong, approaching almost the end point of the scale. (Only 7% of uncharged substituents[2] show higher values, and most of them are rather exotic.) Since nitro compounds are easily available, this group has been of decisive importance in formulating and verifying the validity of the Hammett equation; in fact an irregular effect of some weaker substituents, may be masked by the strong effect of the nitro group. This group has always been present in any set of substituents recommended for studies of reactivity or other properties, the so-called minimum basis set.[15]

Table 2 Some selected values of substituent constants σ for the nitro group

Constant	Assumed substituent effect	Representative values	Kind of determination[a]
σ_m	*I* + reduced *M*	0.71	Statistical[3]
		0.71	'Preferred[2]'
		0.71	p*K* in water[3]
σ_p	*I* + *M*	0.81	Statistical[3]
		0.78	'Preferred[2]'
		0.78	p*K* in water[3]
σ_p^-	*I* + enhanced *M*	1.23	p*K* aniline[3]
		1.28	p*K* phenol[3]
$\sigma_I \equiv \sigma_F$	*I* or *F*	0.76	p*K* acetic acid[3]
		0.68	p*K* quinuclidine[3]
		0.78	*b*
		0.65	Indirect[2]
		0.64	^{19}F NMR shift[2]
		0.66	Calculated[18]
σ_R°	*M* 'normal'	0.17	IR intensity[3]
		0.13	Indirect[2]
		0.0	Indirect[19]
		0.16	^{19}F NMR shift[2]
		0.19	Calculated[20]
σ_R^-	*M* enhanced	0.46	Indirect[15]
σ_R^+	*M* reduced	0.0	Empirical[22]
$\sigma_{\chi-}$	Electronegativity	0.40	Calculated[26]
		0.46	Calculated[22]
σ_α	Polarizability	−0.26	Calculated[22]

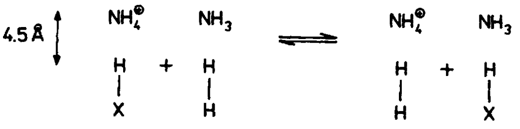
[a] Secondary literature sources are cited wherever possible. [b] From 4-nitrobicyclo-[2.2.2]octanecarboxylic acid.[3]

The use of *meta*- and *para*- substituted derivatives of benzene as model compounds has the rationale that direct steric interaction is eliminated.[1] An additional constraint for the validity of the Hammett equation is the absence of direct resonance between the substituent and the reaction centre ('through resonance' as in *p*-nitroaniline). If this constraint is abandoned, the so-called dual constants are derived,[1] denoted σ^+ or σ^-. In the case of the nitro group only σ^- values come into consideration. According to Table 2 they are rather different from normal σ_p: the difference is usually explained in terms of resonance described by the canonical structure **11**. Accordingly, the normal constants σ_p are also assumed to be composed of an inductive and a smaller resonance part and enormous effort has been given to their quantitative separation.[1,2] In the case of the nitro group the inductive effect is evidently much more important and any kind of separation must begin with it.

4.2 Inductive Substituent Effect

Evaluation of a more or less purely inductive effect requires the replacement of the benzene ring considered for the Hammett equation by a rigid alicyclic system[1] such as bicyclo[2.2.2]octane or quinuclidine. Remarkably, even simple aliphatic systems, for instance derivatives of acetic acid, give concordant results: the direct steric interactions are negligible for common substituents.[16] The resulting constants are denoted as inductive, σ_I, but some authors[2] prefer the term field constants, σ_F. However the question of how the effect is transmitted is immaterial and in fact ill formulated.[17] More important is the fact that several model systems give the same relative result, as shown for the NO$_2$ group in Table 2. To obtain numerically concordant results each kind of the substituent constant must be multiplied by normalizing factors. Therefore, the agreement in Table 2 depends also on these factors which in turn depend in part also on the nitro group itself. The agreement for one substituent does not tell much; any disagreement could be observed only if the behaviour of the nitro group were rather different from that of the other substituents. This is not the case: again the effect of NO_2 is strong and regular.

A purely theoretical approach[18] to the inductive effect uses pseudo-molecules with a non-bonded substituent at a fixed distance: for instance the enthalpy of the isodesmic reaction, equation (1), can be calculated. Even here the resulting constants must be normalized. Examples of these results are given in Table 2 as 'calculated' values.



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4.3 Mesomeric (Resonance) Effect

Since the inductive effect is omnipresent, any evaluation of the mesomeric effect always means that two similar systems need to be compared.[1] When the inductive effects can be assumed to be equal, the mesomeric effect is obtained by subtracting the two values. In the case of the NO_2 group the inductive effect is strong, and subtracting two almost equal values is not dependable, as stated in classical textbooks. However, the pioneering work of Taft[15] yielded a resonance constant σ_R, small compared to σ_I but not negligible (Table 2). The calculation was complex; the two systems compared were substituted acetic acid esters and substituted benzoic acids; the inductive effects were not equal and were normalized with reference to bicyclo[2.2.2]octane-1-carboxylic acids.

One of the present authors tried to improve this normalization with the result that the mesomeric effect of the nitro group is near to zero in benzoic acids;[19] it was concluded that even the resonance in nitrobenzene corresponding to the canonical structures **8**, **9** and **10** has almost zero weight with respect to the accuracy of common experimental approaches. This finding was strongly opposed[15,21] but was later rediscovered by Taft himself and used particularly for gas-phase acidities.[22] With benzoic acids as models, it is probably not possible to obtain more accurate results, nor to decide whether the effect is small or 'practically zero'.

This picture is changed when substituted phenols or anilines are used as model compounds. From the constants σ_p^- one can define constants σ_R^- which are certainly not zero (Table 2). These constants describe the substituent effect of the nitro group in several similar systems and can be compared with the effects of other acceptor groups; hence they could be accepted as a measure of the resonance effect. Evidently, the canonical structures **8**—**11** are much more important for derivatives with a conjugated electron-donating group. These results were independently confirmed by a novel approach, based on determination of the weights of canonical structures from experimental bond lengths,[23] the so-called HOSE model. The results obtained for *p*-nitroaniline, its *N*,*N*-diethyl derivative and *p*-nitrophenolate anion are given in Table 3 and compared with those for nitrobenzene. In order to use nitrobenzene as a reference, for which there is no possibility of forming structure **11** by a through-resonance effect, only structures **6**—**10** were considered for all the compounds. Since the N–O bonds are rather insensitive to substituent effects in which the nitro group is involved, the N–O bonds were not considered in the calculations. Even if the HOSE estimates of the weights of canonical structures are only approximate, it is clear that a considerable change of the resonance effect is observed when comparing nitrobenzene and the *p*-nitrophenolate anion: an increase from 40 to 51% for the sum of the weights of **8**, **9** and **10** is observed. It is significant that structure **10**, with a symmetrical (C_2) localization of double bonds, increases most significantly (from 13 to 21%). This may be connected with two additional kinds of interactions: (*i*) a contribution of structure **11** which yields the same changes in geometry of the system under study, and (*ii*) an important contribution of a structure, in which the field effect of the nitro group causes the lone pairs of electron-donating substituents to interact more strongly with the π-system of the ring.[4,5,22] We conclude that the real structure of these *para*-derivatives is described not only by structures **6**, **6a**, **7** and **7a**, which indicate no resonance between the nitro group and the ring, but also by relatively large contributions of the canonical structures **8**, **9**, **10** and **11**. An analysis of the geometry of nitrobenzene[11] reveals negligible resonance, even if the weights of the appropriate canonical structures are not exactly equal to zero (Table 3). The same applies for several other acceptor substituents.

Table 3 Weights of canonical structures indicating resonance interactions in nitrobenzene and its derivatives (HOSE model).[23]

Molecule[a]	Weights of canonical structures				
	6 + **6a**	**7** + **7a**	**8**	**9**	**10**
NB	29.9	29.9	13.3	13.3	13.5
*p*NA	26.1	26.9	14.4	14.5	18.2
*p*NPhA	24.7	24.0	15.2	14.9	21.3
D*p*NA	26.3	26.3	14.1	14.1	19.1
3,5-DNXy	28.6	28.6	13.6	13.6	15.8
2,6-DNXy	30.1	30.1	12.9	12.9	14.1

[a] *Abbreviations*: NB: nitrobenzene; *p*NA: *p*-nitroaniline; *p*NPhA: *p*-nitrophenolate anion; D*p*NA: *N*,*N*-diethyl-*p*-nitroaniline; 3,5-DNXy: *N*,*N*-dimethyl-4-nitro-3,5-xylidine; 2,6-DNXy: *N*,*N*-dimethyl-4-nitro-2,6-xylidine.

Note that some physicochemical values have been used to evaluate the mesomeric effect directly. For instanct the IR intensity of the ν_{16} band in mono-substituted benzenes[24] was used thus. The value of σ_R^0 for NO_2 is not zero (Table 2) but it is not certain whether it is not influenced slightly also by the inductive effect: this could be of importance just for NO_2.

A theoretical model for the resonance effect may be based on the extent of withdrawal of electronic charge from the ring by substituents in mono-substituted derivatives of benzene. STO-3G calculations[25] for the nitro group yield a non-zero value of 0.13 which is lower than that in Table 2 which was obtained from nitroethene as a model.[20] As well as depending on the model, these kinds of values must depend also on the basis set used for calculations. For more reliable results it may be necessary to take electron correlation into account.

4.4 Other Substituent Effects

Electronegativity constants[26] are still somewhat mysterious and have been used very rarely, as have polarizability constants[22] also (Table 2). The steric constants of the nitro group have been less extensively studied, the hydrophobic constants a little more: for the values see ref. 27. All these effects are overshadowed by the strong polar effect.

5 Pro and Cons for Resonance Effects in Nitrobenzene Derivatives

5.1 Problem Statement

As seen already in previous sections, there is a serious dispute concerning the importance of resonance in nitrobenzene derivatives. Many arguments have been brought together from various areas outside the framework of the theory of substituent effects. For this reason we give a brief review in a separate section. Evidently the results will be different for nitrobenzene itself and for its derivatives with an electron-donating substituent in a conjugative position.

5.2 Theoretical Calculations

The effect of the nitro group on the rest of the molecule and on global or local properties may be described by the energies of the lowest unoccupied and highest occupied molecular orbitals, LUMO and HOMO, and by the global charge distribution. These may all be obtained from molecular orbital calculations.

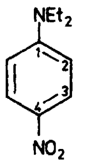
Ab initio calculations on nitrobenzene with optimization of geometry at the 6-31G level[28] gave the following extents of withdrawal of the electronic charge from the ring: 0.521 for σ electrons, 0.067 for π electrons, with a total charge transfer of 0.588. Other calculations using different basis sets[25,28–30] have given a similar picture. On considering the π-electron charges, it is immediately clear that typical resonance structures which may be drawn for nitrobenzene **6**—**10** are realistic but the effect is not too large.

However this statement does not fit with the total electron charges: of all carbon atoms only C-1 is positively charged. The point is that all hydrogen atoms are a source of electrons for the carbon atoms to which they are attached.

5.3 Structural Arguments

Analysis of the geometry of nitrobenzene[11] leads to the conclusion that the mesomeric effect of the nitro group on the ring is very small. This conclusion is essentially in line with the above-mentioned quantum chemical calculations which either oppose the existence of this effect[29] or indicate its rather low value.[28,30]

The situation is quite different for *p*-nitrobenzene derivatives with electron-donating substituents leading to a push–pull effect. Valence bond calculations for *p*-nitroaniline and *p*-nitrophenol yielded very low weights for structure **11** (<1.0%)[5] but, on the other hand, an analysis of the geometry of *N,N*-diethyl-*p*-nitroaniline **12**, *N,N*-dimethyl-4-nitro-3,5-xylidine **13** and *N,N*-dimethyl-4-nitro-2,6-xylidine **14** leads to the conclusion[8] that the steric effect of methyl groups in positions 3 and 5 disturbs the geometry of the N–Ph–N fragment significantly less than their action from positions 2 and 6.



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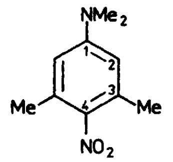

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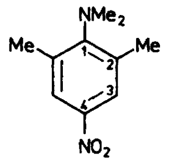

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Thus, the only conclusion may be that the contribution of the structure **11** is important in descriptions of the molecular geometries of **12**, **13** and **14**. This is well illustrated by a significant decrease of the sum of the weights of (**8** + **9** + **10**) from 47% for **12** to 43% for the 3,5-derivative and down to 40% for the 2,6-derivative, which is comparable to 40.1% for nitrobenzene itself.

Further, indirect support for the through-resonance effect in *para*-substituted derivatives of nitrobenzene comes from the good linear dependencies of the weights of various canonical structures on σ_{p} or σ_{p}^{+} of the conjugated substituents.[9] For the canonical structure **11** the correlation coefficient *r* is −0.934 for 14 data points; not much worse are *r*-values for similar scatter plots with other canonical structures.

5.4 Discussion of Dipole Moments

A classical argument for resonance originates from the dipole moment of nitrobenzene, which is greater than that of nitromethane or 2-nitro-2-methylpropane (Table 4). The difference was called the mesomeric dipole moment.[31] Moreover, in 2,4,6-trimethylnitrobenzene possible resonance is suppressed and the dipole moment is actually reduced.[32] However convincing this reasoning appears, it can be challenged when a more complete series of derivatives is compared[33] (Table 4). With increasing size of molecules of aliphatic and alicyclic nitro compounds, their dipole moments increase owing to pure induction; ultimately they exceed the value for nitrobenzene. On the other hand, the dipole moments of 2,4,6-trialkylnitrobenzenes decrease continuously with increasing size of the alkyl group, although a further efficient hindrance to resonance is no longer possible. (At a twisting angle of say 70° the resonance is practically inhibited.) These facts can be understood in terms of induction, either within the alkyl group of RNO_2 or in the *ortho*-alkyl groups of $C_6H_2R_3NO_2$, but a quantitative estimation is hardly possible. In any case the simple difference between an aliphatic and an aromatic derivative cannot be taken as a measure of the mesomeric effect: any resonance in nitrobenzene has not been proven from dipole moments.

Table 4 Experimental dipole moments of some nitro compounds (in Debye)[a]

R	RNO_2	2,4,6-$R_3C_6H_2NO_2$
H	—	3.97
Me	3.16	3.65
Et	3.21	—
Pr^i	3.31	3.59
Bu^t	3.42	3.45
Cyclo-C_6H_{11}	3.53	3.46
1-Adamantyl	3.55[b]	—
4-Adamantyl	3.76[b]	—
1-Diadamantyl	4.03	—
Ph	3.97	3.40

[a] Benzene solution, 298 K, data from ref. 33 unless otherwise noted. [b] Ref. 34.

5.5 Correlation of Reactivity Data

This matter was summarized recently,[35] and has been a subject of much disputation,[15,16,19,21] proceeding mostly in terms of substituent constants and not always in an understandable way. The indisputable experimental fact is an approximate linear relationship between p*K* values of substituted benzoic acids, for *para*- *vs*. *meta*-derivatives with the same substituent. It is valid for substituents NO_2, CN, SO_2X, CF_3, CCl_3, CH_2Hal and others (only with slight deviations also for COX), in aqueous systems,[19] non-aqueous solvents,[36] and the gas phase,[35] not only for p*K* values, but also for rate constants of various reactions.[19] Conjugated substituents, like OR, NR_2 and halogens, deviate very distinctly. The slopes of corresponding linear plots show that the substituent effect is somewhat stronger from the *para*- than from the *meta*-position. The simplest explanation is that all these substituents act by a single main mechanism: it is merely a question of terminology whether it is called simply the inductive effect. Within the benzene nucleus the so-called π-inductive effect[19] may be operative, explaining the greater effect in the *para*-position; this is in agreement with some quantum chemical calculations.[37] The opponents of this idea argued that the mesomeric effect must be present but that it is proportional to the inductive effect for all named substituents.[15,16] This cannot be directly disproved: the problem is how such a general proportionality can come to exist for such different structures. Essential for the reasoning is the linearity of the plot, not its slope. Attempted proof that the slope is sometimes less than unity[16] has a statistical defect: omitting the point for hydrogen (origin of the coordinates) made it impossible to determine the slope reliably.

Concluding this discussion, we offer the opinion that the presence or absence of resonance must be considered with respect to an observable quantity and to its accuracy. With this in mind we find practically no resonance in nitrobenzene but can observe it in derivatives like 4-nitroaniline or 4-nitrophenolate anion, the extent of the observed resonance effect being dependent on the electron-donating power of the *para*-substituent. An evident resonance effect of the nitro group is observed in the case of nucleophilic substitution but particularly in the case of vicarious nucleophilic substitution of hydrogen,[38] for which it is a *sine qua non*.

6 Conclusions

The nitro group is an outstanding substituent which should be included whenever possible in studies of substituent effects: its effects are strong and can be quantitatively estimated with reliability. On the other hand, the theoretical interpretation of these effects is not always unambiguous, particularly the existence of resonance.

The idea of separating inductive and resonance effects evidently has its limits and the term resonance should generally be used in a quantitative sense with respect to certain observable quantities Resonance is certainly not present, or at least not observable, in every single case where resonance formulae have been written in the literature

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